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(54) **PREPARATION ET UTILISATION D'OPACIFIANTS MIXTES A BASE D'OXYDES DE TITANE ET DE SILICIUM**
(54) **PREPARATION AND USE OF MIXED OPACIFIERS BASED ON TITANIUM AND SILICA OXIDES**

(57)

The invention concerns a method for preparing a composition based on TiO₂ useful as opacifier which consists in mixing with an aqueous TiO₂ dispersion an aqueous dispersion of at least an inorganic spacer, in conditions such that the two mineral species combine into mixed mineral flocs wherein the TiO₂ particles are globally spaced from one another by the spacer particles and/or aggregates. The invention also concerns a composition based on TiO₂ and SiO₂ characterised in that the TiO₂ and SiO₂ particles are combined therein in the form of mixed mineral flocs based on TiO₂ and SiO₂ wherein the TiO₂ particles are globally isolated from one another by said silica aggregates and its use as opacifier, in particular in the paper industry.



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(54) **PREPARATION ET UTILISATION D'OPACIFIANTS MIXTES A
BASE D'OXYDES DE TITANE ET DE SILICIUM**

(54) **PREPARATION AND USE OF MIXED OPACIFIERS BASED ON
TITANIUM AND SILICA OXIDES**

(57) La présente invention a pour objet un procédé de préparation d'une composition à base de TiO_2 utile comme agent opacifiant comprenant le mélange à une dispersion aqueuse de TiO_2 , d'une dispersion aqueuse d'au moins un agent espaceur inorganique, dans des conditions telles que les deux espèces minérales s'agencent en des floes minéraux mixtes dans lesquels les particules de TiO_2 sont globalement espacées les unes des autres par des particules et/ou agrégats de l'agent espaceur. Elle a également pour objet une composition à base de TiO_2 et de SiO_2 caractérisée en ce que les particules de TiO_2 et de SiO_2 y sont agencées sous la forme de floes minéraux mixtes à base de TiO_2 et de SiO_2 dans lesquels les particules de TiO_2 sont globalement isolées les unes des autres par des agrégats de ladite silice et son utilisation à titre d'agent opacifiant notamment en industrie papetière.

(57) The invention concerns a method for preparing a composition based on TiO_2 useful as opacifier which consists in mixing with an aqueous TiO_2 dispersion an aqueous dispersion of at least an inorganic spacer, in conditions such that the two mineral species combine into mixed mineral floes wherein the TiO_2 particles are globally spaced from one another by the spacer particles and/or aggregates. The invention also concerns a composition based on TiO_2 and SiO_2 characterised in that the TiO_2 and SiO_2 particles are combined therein in the form of mixed mineral floes based on TiO_2 and SiO_2 wherein the TiO_2 particles are globally isolated from one another by said silica aggregates and its use as opacifier, in particular in the paper industry.



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(54) Title: PREPARATION AND USE OF MIXED OPACIFIERS BASED ON TITANIUM AND SILICA OXIDES (54) Titre: PREPARATION ET UTILISATION D'OPACIFIANTS MIXTES A BASE D'OXYDES DE TITANE ET DE SILICIUM (57) Abstract <p>The invention concerns a method for preparing a composition based on TiO₂ useful as opacifier which consists in mixing with an aqueous TiO₂ dispersion an aqueous dispersion of at least an inorganic spacer, in conditions such that the two mineral species combine into mixed mineral flocs wherein the TiO₂ particles are globally spaced from one another by the spacer particles and/or aggregates. The invention also concerns a composition based on TiO₂ and SiO₂ characterised in that the TiO₂ and SiO₂ particles are combined therein in the form of mixed mineral flocs based on TiO₂ and SiO₂ wherein the TiO₂ particles are globally isolated from one another by said silica aggregates and its use as opacifier, in particular in the paper industry.</p> (57) Abrégé <p>La présente invention a pour objet un procédé de préparation d'une composition à base de TiO₂ utile comme agent opacifiant comprenant le mélange à une dispersion aqueuse de TiO₂, d'une dispersion aqueuse d'au moins un agent espaceur inorganique, dans des conditions telles que les deux espèces minérales s'agencent en des floes minéraux mixtes dans lesquels les particules de TiO₂ sont globalement espacées les unes des autres par des particules et/ou agrégats de l'agent espaceur. Elle a également pour objet une composition à base de TiO₂ et de SiO₂ caractérisée en ce que les particules de TiO₂ et de SiO₂ y sont agencées sous la forme de floes minéraux mixtes à base de TiO₂ et de SiO₂ dans lesquels les particules de TiO₂ sont globalement isolées les unes des autres par des agrégats de ladite silice et son utilisation à titre d'agent opacifiant notamment en industrie papetière.</p>		

PREPARATION AND USE OF MIXED OPACIFIERS BASED ON TITANIUM AND SILICA OXIDES

The object of the present invention is a compound with a TiO_2 base for use as an opacifying agent, specifically in laminated papers, and a preparation process that enables the composition to be obtained.

Laminated paper, commonly referred to as decorative paper, is the surface element having both opacity and decorative function used in the manufacture of laminated panels designed for use in the furnishings industry.

A particularity of decorative paper is that it possesses an extremely high percentage of TiO_2 , possibly up to 40% of the mass of the dry sheet.

Printing and writing papers, by comparison, may contain an absolute maximum of 10%.

The level of opacity required for decorative paper in fact explains this high TiO_2 content. The paper undergoes a resin bonding process that renders it transparent. As this is incompatible with its opacifying and decorative purposes, this must be remedied by the addition of an opacifying agent.

Titanium dioxide is traditionally used for this application because it is the only white pigment that, due to its high refraction index, can provide the required levels of opacity.

Application WO 89/08739, however, suggests replacing the TiO_2 at a rate of 5 to 40 wt-% with precipitated amorphous silica and to use the corresponding mixtures as charges in the paper industry because they are more economical.

Sheets of paper are conventionally prepared from a mixture of cellulose fibers and mineral charges containing mostly TiO_2 dispersed in water. This mixture is contained in a "breastbox" which feeds a canvas where the sheet is formed by draining and filtration. During filtration, the cellulose fibers and a portion of the mineral charge are retained on the canvas, whether or not there are interactions with the entangled fibers. A "fiber mat" is thus obtained which, after drying, results in a sheet of paper.

It has been proven, in fact, that only a portion of the initial quantity of TiO_2 is retained in the fiber mat, and that additionally this fraction is generally too agglomerated for the TiO_2 to develop maximum opacity.

In order to reduce this loss of TiO_2 during formation of the fiber mat, paper manufacturers generally introduce retention agents into their cellulose mixtures. These agents are conventionally cationic polymers which enable fixation of the TiO_2 particles onto the fibers through homo- and hetero-flocculation phenomena.

However, in the case of retention of opacifying charges such as titanium dioxide, the use of an electrically charged polymer results in loss of opaque efficiency due to overly extensive and overly dense flocculation.

As a result, it appears that simply retaining TiO_2 in the fiber mat is not sufficient in and of itself in terms of the rate of opacity. It would also be necessary to retain the TiO_2 in the fiber mat in a sufficiently dispersed form that it would be able to retain its pigmentary properties and develop good opacifying power. Advantageously, it would then be possible to obtain the same opacity while binding less TiO_2 . The opacity rate of the TiO_2 would be significantly increased thereby.

To that end, the international patent application WO 97/18268 proposes a process for treating the surface of TiO_2 particles. Treatment consists of covering them with a single layer of mineral particles, such as silica, whose grain size is less than that of TiO_2 particles. This single particle layer coating makes it possible to space the TiO_2 particles away from each other.

The object of the present invention is specifically to propose a new compound with a TiO_2 base that meets all the aforementioned requirements.

More specifically, it proposes a new opacifying agent system that makes it possible to both improve the retention of TiO_2 during formation of the fiber mat and to keep it in a flocculation structure that is the least detrimental possible to opacity.

The inventors have also demonstrated that a solution to the problem of agglomeration of the mineral charge consists of creating mixed mineral congregates by inserting particles of an agent called an inorganic spacer, whether or not in aggregate form, between the TiO_2 particles.

The mixed mineral congregates obtained according to the invention are advantageous for several reasons:

- they allow the TiO_2 particles to remain sufficiently dispersed during the various steps in the formation of the sheet of paper such that a maximum thereof can develop their pigment characteristics and thus contribute to the opacity of the dry sheet,
- they have an open structure, favorable to better retention,
- they also have proved to be sufficiently resistant to resist the capillary forces that develop during the draining and drying of the fiber mat, as well as the shearing that may occur during the manufacture of a sheet.

In fact, the internal cohesion of the mixed mineral congregates resulting from the association of at least one inorganic spacer with TiO_2 is based on the solidity of the ionic bonds established between the TiO_2 and the spacer. This cohesion results directly from the process adopted to prepare the mixed mineral congregates.

More precisely, these congregates are obtained under operating conditions such that the TiO_2 and the inorganic spacer in question have opposite and significantly different surface charges. Specifically, the TiO_2 and the inorganic spacer in question must have isoelectric points sufficiently different for there to be a pH range in which these two types of minerals have opposite charges. Under these conditions, the two types of minerals are electrostatically attracted to each other. The resultant forces of attraction must be sufficient to yield a structural arrangement of the two compounds on the one hand, and to stabilize them in this form on the other.

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Consequently, the first object of the present invention is a process for the preparation of a compound having a TiO_2 base that can be used as an opacifier that includes steps according to which:

- an aqueous dispersion of at least one inorganic spacer is mixed with an aqueous dispersion of TiO_2 , with the mixture of the two dispersions performed under agitation and at a pH between the respective isoelectric points of the TiO_2 and the spacer and selected such that the TiO_2 and the spacer have opposite and sufficiently different surface charges to result, under the effect of electrostatic forces, in their arrangement into mixed mineral congregates in which the TiO_2 particles are globally spaced away from each other by the particles and/or aggregates of the spacer;
- as necessary, the pH is adjusted to the value established in Step 1,

with the process characterized in that it also includes the steps according to which:

- the resultant aqueous dispersion of mixed mineral congregates is cured at a temperature sufficient to reinforce the solidity of the bonds established between the TiO_2 particles and the particles and/or aggregates of the spacer,
- the compound is recovered in the form of an aqueous dispersion of mixed mineral congregates, and
- the compound can possibly be formulated in dry form.

Figure 1 schematically depicts the structure of mixed mineral congregates obtained according to the invention. It is confirmed by the transmission electron micrograph, shown in Figure 2.

As defined in the invention, the term "congregate" means the mixed agglomerates of the two kinds of minerals of the TiO_2 type and an inorganic spacer, SiO_2 , for example. These agglomerates result from the association between the aggregates of the spacer and the TiO_2 particles.

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A spacer is composed of particles or aggregates of particles which insert themselves between the TiO_2 particles.

As for the isoelectric point, it is the pH for which the particle of the type of mineral in question has a net surface charge of zero. For a pH greater than this value, the net charge is negative; and for a lower pH, the net charge is positive.

The TiO_2 used according to the invention is preferably a rutile TiO_2 .

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More preferably, it is a rutile TiO_2 of pigment size.

If warranted, it may be coated with an mineral surface treatment.

This surface treatment preferably contains at least one compound chosen from among alumina, silica, zirconia, phosphate, cerium oxide, zinc oxide, titanium oxide, and mixtures thereof.

The quantity of oxide(s) can be 1 to 20 wt-% or less, or preferably on the order of 3 to 10 wt-% or less, in relation to the total pigment weight.

As examples of these titanium dioxides, the two rutile pigments Rhoditan RL18 and RL62, manufactured by Rhône-Poulenc, may be cited specifically. These two pigments are differentiated by the composition of their surface treatment and the resultant Zeta potentials.

RL18 has a silica/alumina surface treatment ($\text{SiO}_2/\text{Al}_2\text{O}_3$) and a negative Zeta potential at pH 6, and is called "anionic TiO_2 ".

RL62 has a phosphate/alumina surface treatment ($\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3$) with a positive zeta potential at pH 6, and is called "cationic TiO_2 ". The choice of pH = 6 approaches the pH for industrial use.

In the present invention, the selection of anionic or cationic TiO_2 is, of course, determined by the choice of the inorganic spacing agent associated therewith.

In each case, an inorganic spacing agent with an isoelectric point sufficiently different from that of the TiO_2 in question is chosen so that the electrostatic attractions between the two compounds, necessary for their arrangement, may occur.

The aqueous dispersion of TiO_2 used according to the invention contains approximately 5 to 80 wt-% TiO_2 , preferably approximately 5 to 40 wt-%. In this respect, the limiting factor is the viscosity of the suspension, which must remain at a reasonable value in order to be easily handled.

According to a preferred embodiment of the invention, the TiO_2 adopted is a cationic pigmentary rutile TiO_2 , specifically Rhoditan RL62.

As for the inorganic spacing agents considered according to the invention, they must not interfere with the other reagents traditionally used in the paper industry.

Preferably, they do not significantly absorb any visible light.

In general, their particle size is smaller than that of the TiO_2 particles. However, these particles are preferably used in the form of aggregates with a size which is thus larger than that of the TiO_2 particles. The aggregates are preferably between approximately 0.5 and 2 μm in size.

As examples of inorganic spacing agents that can be used according to the invention, the following can be specifically cited: silicon, titanium, zirconium, zinc, magnesium, aluminum, yttrium, antimony, cerium and tin oxides; barium and calcium sulfates; zinc sulfide; zinc, calcium, magnesium, lead and mixed metal carbonates; aluminum, calcium, magnesium, zinc, cerium and mixed metal phosphates; magnesium, calcium, aluminum, and mixed metal titanates; magnesium and calcium fluorides; zinc, zirconium, calcium, barium, magnesium, mixed alkaline-earth, and silicated mineral silicates; alkaline and alkaline-earth aluminosilicates; calcium, zinc, magnesium, aluminum, and mixed metal oxalates; zinc, calcium, magnesium and alkaline-earth aluminates; aluminum hydroxide, and mixtures thereof.

The spacing agent, of course, is selected such that it has an isoelectric point sufficiently different from the TiO_2 form adopted.

As inorganic spacing agents particularly suitable for the present invention, the following inorganic oxides may be cited, chosen preferentially from among silicon, zirconium, aluminum, antimony, cerium, and tin oxides and mixtures thereof.

In the specific case wherein the cationic pigmentary rutile TiO_2 is adopted, the preferred inorganic spacing agent is a silica, an alumina, a silicoaluminate, or a mixtures thereof.

The ratio between the TiO_2 and the spacing agent is variable, of course, depending on the kind of spacing agent adopted.

The lower limit of this ratio is formed in general by the minimum quantity of the inorganic spacing agent necessary to observe a positive effect in the level of opacification, and its upper limit by the maximum quantity of spacing agent beyond which undesirable effects would appear at the level of paper incorporating the compound obtained according to the process claimed. These undesirable effects can translate specifically into paper fragility, particularly in terms of resistance whether in dry state or wet state.

This spacing agent can generally be used at a rate of approximately 1 to 40 wt-% in relation to the weight of TiO_2 , preferably at a rate of approximately 5 to 15 wt-%, and even more preferably at a rate of approximately 10 wt-%.

As explained above, the two compounds are brought together in the form of corresponding aqueous dispersions under operating conditions developed by the heterocoagulation of TiO_2 with particles and/or aggregates of particles from the inorganic spacing agent, the mixed mineral congregates. The spacing agent can also be precipitated in situ. In that case, the pH favoring heterocoagulation will be adjusted after the step precipitating the spacing agent.

These operating conditions favorable to the appearance of heterocoagulation between the inorganic spacing agent and TiO_2 are notably the choice of a pH in a range defined by their respective isoelectric points. It is advisable to select a pH such that the two compounds have opposite and sufficiently different surface charges.

For operational reasons, it is desirable that the isoelectric points of the spacing agent and the TiO_2 be spaced at least one pH unit apart.

The mixed mineral congregates comprising the expected compound are thus formed under agitation of the dispersions, generally at ambient temperature and at a pH as defined above. If necessary, the pH may have to be adjusted during reaction in order to maintain a value favorable to the formation of the congregates.

Attraction is immediate. However, it is preferable to continue agitation for approximately 15 minutes in order to stabilize the system prior to the curing stage.

According to a preferred variant of the invention, TiO_2 is used in cationic pigmentary rutile form and is preferably RL62®, and the associated spacer is silica.

Even more preferably, the silica used is a silica with a large specific surface between 20 and 300 m^2/g . It may assume the form of aggregates that are between approximately 0.5 and 10 μm in size.

The use of silica as a spacing agent according to the present invention is advantageous at for several reasons.

First, it has an isoelectric point in the neighborhood of 2, which is a value sufficiently different from that of the isoelectric point of the cationic form of TiO_2 (6.5 to 7).

Additionally, silica has the advantage of not significantly adsorbing visible light, which is favorable to sheet whitening.

The pH for exposing the two corresponding dispersions to each other is between the isoelectric points of the spacing agent and the TiO_2 . The isoelectric point of the TiO_2 in question normally imposes the upper limit, and the isoelectric point of the spacing agent utilized should impose the lower limit. In the present case, this pH should fall between 2 and 6.5. However, in the particular case of RL62, it is necessary to avoid dissolution of its surface treatment. To achieve this, the pH range would be limited to between 4.5 and 6.5. Even more preferably, the process according to the invention is implemented at a pH of approximately 5.5.

In the specific case of preparation of a compound containing TiO_2 in cationic pigmentary rutile form linked to aggregates of silica particles, silica is used at a rate of at least 1 wt-% in relation to the weight of TiO_2 .

It is only with this amount of silica that a significant gain in opacity retention begins to occur. This amount of silica can be increased to approximately 20 wt-% of TiO_2 . Above that, the problem of paper fragility described above is encountered.

Consequently, silica is preferably used at a rate of approximately 5 to 15 wt-% of the weight of TiO_2 , even more preferably at 10 wt-%.

The silica can be introduced either in the form of a slurry-type aqueous dispersion of silica particles or can be generated in situ by acidification of a silicates solution.

In the specific case wherein the silica is precipitated in situ in the TiO_2 dispersion, following the precipitation step, the reaction milieu is adjusted to a value favorable to the manifestation of electrostatic forces between the TiO_2 and the silica thus generated. These forces are necessary to their heterocoagulation.

The second step required according to the process claimed is in fact an operation to cure the mixed mineral congregates formed in the previous step.

As previously mentioned, the mixed mineral congregates obtained according to the process claimed are specifically designed to be used as an opacifying agent in the paper making industry. This involves an entire succession of handling of the congregates.

Consequently, it is necessary that these congregates be solid enough to resist shearing, and if the case arises, the flocculating effect of polymer derivatives such as PAE (polyamino-amide-epichlorohydrin) and the withdrawal of water during the formation and drying of the sheet.

It is important, then, that the TiO_2 particles present in the compound obtained according to the invention be not only sufficiently dispersed in order to improve their opacity, but also better retained during sheet formation.

As a consequence, the curing operation performed according to the process claimed is proving to be particularly advantageous to the strengthening of chemical, even steric, actions established within mixed mineral congregates. Moreover, it is probable that some of the ionic bonds are converted into covalent bonds at the conclusion of this curing step.

In the specific case of preparation of a compound of mixed mineral congregates having a TiO_2 and SiO_2 base, this curing step is performed at a

temperature higher than 40°C. Preferably, the temperature is between approximately 60°C and 100°C.

Heating time lasts at least 30 minutes and, if necessary, can be prolonged up to three hours. At the conclusion of the heating step, the resultant compound is allowed to cool to ambient temperature and may be recovered as is.

The compound may be used directly in that form as an opacifying agent.

However, it is also conceivable to formulate it in dry form. To this end, it has proved possible to apply conventional drying techniques to the dispersion obtained according to the invention.

In particular, this may be spray drying or thin-film drying. However, simple drying will not result in a suitably redispersed product. Since the conglomerates clump during drying, it is preferable to pulverize the product using an air-blast grinding step (micronization).

According to another variant of the process claimed, the mixed mineral conglomerates obtained at the conclusion of the first or second step of the process may undergo a mineral surface treatment. This includes at least one hydrated oxide as defined earlier. These latter may be precipitated in a reaction milieu after the TiO_2 and spacing agent dispersions are exposed to each other.

The mineral surface treatment represents approximately 16 wt-% or less, or preferably approximately 10 wt-% or less, of the total weight of the mixed mineral conglomerates so treated.

The present invention covers TiO_2 -based compounds that can be obtained according to the process claimed.

Another object of the present invention is a compound having a TiO_2 and SiO_2 base, characterized in that the TiO_2 and SiO_2 particles are arranged therein in the form of mixed mineral conglomerates wherein the TiO_2 particles are globally spaced away from each other by the aggregates of the silica.

These mixed TiO_2 and SiO_2 conglomerates are stabilized through the electrostatic forces established between the TiO_2 particles and the SiO_2 aggregates. Moreover, the stability of the mineral conglomerates is reinforced by the fact that they undergo the curing described earlier. This curing operation

particularly contributes to the creation of covalent bonds between the TiO_2 and SiO_2 within the congregates.

In the case of the mixed mineral congregates according to the invention, there is no uniform distribution of the aggregates of the inorganic spacing agent around the TiO_2 particles. This distribution is discontinuous. Figures 1 and 2 give a representation of the structure of the congregates.

The preferred TiO_2 is a rutile TiO_2 of pigmentary size.

If need be, it can be coated with a mineral surface treatment. This surface treatment can be chosen from among phosphates, alumina, silica, zirconia, cerium oxide, zinc oxide, titanium oxide, and mixtures thereof.

The quantity of oxide(s) may be approximately 1 to 20 wt-% or less, or preferably approximately 3 to 10 wt-% or less in relation to the total pigment weight.

The preferred TiO_2 is a cationic pigmentary rutile TiO_2 .

The preferred TiO_2 is RL62.

The silica used is more preferably a silica having a large specific surface, specifically between approximately 20 and 300 m^2/g . It is present in the form of aggregates the sizes of which are between approximately 0.5 and 10 μm . The preferred silica is a precipitation silica. It can also be a silica generated in situ by acidification of a silicates solution.

The silica is preferably present at a rate of approximately 1 to 20 wt-% of the weight of the TiO_2 , and preferably at a rate of approximately 5 to 15 wt-%, and even more preferably 10%.

If need be, these TiO_2 and SiO_2 -based mineral congregates may be coated with at least one mineral surface treatment as defined above.

The quantity of mineral surface treatment may be approximately 16 wt-% or less, preferably approximately 10 wt-%, in relation to the total weight of the mixed mineral congregates.

The compounds defined above or obtained according to the invention are proving interesting in the preparation of paper including laminated paper, and particularly advantageous in terms of retention of the TiO_2 at the cellulose fiber level and the opacity rate of the TiO_2 used.

The conventional process for preparation of laminated paper or decorative paper generally uses, in addition to anionic cellulose fibers and the opacifying agent, a polymer agent that is cationic in nature as a reinforcing agent in the wet state and a retention agent.

In the case wherein a compound based on $\text{TiO}_2/\text{SiO}_2$ mineral congregates is used as an opacifying agent, it is observed that chemical retention by electrostatic attraction is advantageously strengthened in comparison to TiO_2 in individual cationic form.

This amplification of retention can be explained in the following manner:

In the absence of a cationic polymer, the cationic TiO_2 is attracted by the anionic cellulose fibers, which is favorable to TiO_2 retention. In contrast, in the presence of the polymer, the fiber- TiO_2 interactions change and TiO_2 retention decreases. This phenomenon translates into cationization of cellulose fibers, resulting from their being covered by the cationic polymer.

Conversely, in a compound whose base is $\text{TiO}_2/\text{SiO}_2$ mineral congregates, there is a mixture of cationic TiO_2 and anionic SiO_2 charges whose net zeta potential is negative. The mixed mineral congregates thus behave like anionic charges. Under these conditions, it can be assumed that the mixed congregates can enter into an attractive interaction with the cellulose fibers made positive by the cationic polymer, through the negatively charged silica aggregates they contain. This results in an increase in retention.

The mixed mineral congregate-based compounds claimed and obtained according to the invention are of particular interest as an opacifying agent, particularly in the paper manufacturing industry.

The increased opacity measured on sheets prepared using a mixed mineral congregate-based compound according to the invention visibly results from the accumulation of two phenomena: an increase in the quantity of TiO_2 retained on the paper sheet which results in better retention at the time the fiber mat is formed; and improved opaque capacity resulting from the better dispersion of the titanium particles contained in the congregates.

Further, it was noted that these compounds increase the whiteness of the paper in which they are incorporated.

In addition to this application in the paper manufacturing industry, the compounds claimed and obtained according to the invention are also advantageous when used as opacifying agents in the paint and plastics industries.

The examples and figures in the following are presented by way of illustration and do not restrict the present invention.

Figures

Figure 1: schematic depiction of TiO_2 pigments spaced by SiO_2 aggregates.

Figure 2: transmission electron micrograph of mixed mineral conglomerates with TiO_2 and SiO_2 base.

Figure 3: change in the charge retention for different mixed minerals as a function of agitation speed imposed on the "cellulose/PAE/charge" mixture before formation of the fiber mat.

MATERIALS AND METHODS

Products utilized are commercial products:

- The titanium dioxide used in the examples is rutile titanium dioxide sold under the name of Rhoditan RL62 by the Rhône-Poulenc company. This pigment is formed of rutile TiO_2 coated by a surface treatment of aluminum phosphate ($\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3$). It has a positive zeta potential at pH 6. Its isoelectric point is between approximately 6.5-7.
- Cellulose fibers: dry sheets with a 70/30 mixture of short/long fibers previously refined at 35° SR, supplied by the Arjo Wiggins company.
- The silica is a precipitation silica with a high specific surface of between 20 and 300 m^2g^{-1} having agglomerates between 0.5 and 10 μm in size.

Its isoelectric point is approximately 2.

- PAE resin (polyaminoamide epchlorohydrin) R4947® from the CECA company.

A. "Test sheet retention" test

Equipment:

- Dispermat® and Pendraulik® rapid dispersers
- Mixing tanks
- "Test sheet retention" machine, Techpap company

Operating Method:

- Preparing the fiber/TiO₂ dispersion

The quantity of TiO₂ slurry or suspension of the product according to the invention necessary to introduce 15 g dry of TiO₂ is added to 15 g of fibers redispersed in 500 ml of deionized water for 10 min in the Dispermat at 3,000 rpm. This takes into consideration the TiO₂ slurry extract or the suspension according to the invention. This addition is carried out in a mixing tank. This is followed by dilution with deionized water to 4 liters.

- Preparing the test sample

A 500 ml test sample of the well-homogenized mixture is decanted into a test tube. With a micropipette, the desired amount of PAE resin is added to it (commercial solution diluted 10 times). The test tube is inverted twice to mix well. This test sample is then introduced into the test sheet retention machine to obtain a sheet.

- Measuring retention

Formation of the sheet is triggered after agitating 30 sec at a speed of 1300 rpm, followed by a 1 sec rest time. The sheet obtained is recovered on the canvas in "lump" form, dried in the drier, then calcined at 800°C.

The ashes obtained are then weighed to approximately 10^{-4} g.

The retention rate is given as: $P2/P1$

$P1$ = weight of charges ($TiO_2 + SiO_2$) in the initial 500 ml removed.

$P2$ = weight of ashes after calcination of the prepared sheet.

B. Test of Opacity

Tests of opacity rate were performed using test sheets fabricated for the purpose of understanding the spatial distribution of the titanium dioxide in the dry sheet.

The test sheets were fabricated according to the operating method described in the paragraph below.

Optical properties of the impregnated and pressed test sheet were also measured according to the method described below.

1. Manufacture of test sheets

i) Formulation of paper pulp

Cellulose: 15 g (which represents 100 parts)

Opacifying compound: 100 parts (expressed in TiO_2), or 15 g

PAE: 0.8% dry in relation to the cellulose

ii) Preparing the pulp: defibering

After moistening in water, the cellulose is torn into small squares by hand. The small cellulose squares are gradually added into 500 ml of water under agitation in the Dispermat bowl at 1000 rpm. After the cellulose is added, the speed is increased to 3000 rpm and agitation is allowed to continue for 10 min.

iii) Opacifying agent/fiber compound mixture

The defibered cellulose is diluted to 1 liter. This is then placed under agitation in a mixer with a paddle. The opacifying compound is added in powder or suspension form, then the mixture is agitated for 5 minutes. Finally, the entire mixture is diluted to 4 liters in order to fabricate sheets of 80 g/m^2 substance.

iv) Manufacture of test sheets

500 ml of well-homogenized suspension is placed into a test tube. PAE (commercial solution diluted 10 times to obtain an acceptable sample volume), i.e., 1 ml is added. The test tube is inverted several times to mix well.

The contents of the test tube are poured into the bowl filled with 6 liters of distilled water to draw off the test sheet. Mixing by bubbling through is performed for 10 sec, followed by a rest of 10 sec, then the sheet is fabricated by extruding under vacuum.

The sheet is then recovered on a felt substrate, then vacuum dried for 7 min.

Then the sheet is weighed precisely and the volume removed adjusted in order to obtain the desired gms substance (rule of three).

If one sheet has the desired gms and no manufacturing defect, it is selected for the remaining operations, i.e., chemical and optical assays:

2. Measuring the ash amount

The quantity of TiO_2 present in the 80 g/m² sheet is measured by calcinating one-third of the test sheet at 800°C for one hour.

The percentage of TiO_2 present in the sheet is calculated thus:

$$\text{amount of ash (\%)} = \frac{M_{\text{after calcination}} - M_{\text{under vacuum}}}{M_{\text{before calcination}} - M_{\text{under vacuum}}}$$

The amount of ash measures the quantity of mineral charges present in the sheet. This determination is made using method NF 03-047 (taken from French Paper, Carton, and Pulp Standards: test methods, volume A, 4th edition, 1985).

3. Measuring the opacity of the impregnated and pressed sheet

i) Preparing melamine formol resin (Inilam resin 3240 from CECA)

400 g of water is heated to 60°C. When the temperature is reached, the pre-weighed 245 g of resin is poured gradually in a continual stream. Once all is solubilized, agitation is allowed to continue at 60°C for 30 min. After cooling, filtration through a 50 µm canvas is performed.

ii) Impregnation – pressing

Strips of paper 7cm by 10 cm are cut. The strips are then impregnated by capillary action by placing them on the resin for 1 min. They are expressed between two glass rods and dried for 2 min in a drier at 120°C.

The strips are impregnated a second time by immersing them in the resin for 1 min. They are expressed between one steel bar and one glass bar. They are dried for 3 min in a drier at 120°C.

These sheets are attached to a substrate formed from bottom to top by 2 white barriers and 3 kraft barriers, with the test sheet in direct contact with the kraft barriers.

The laminates obtained are pressed for 8 min at 150°C under 100 bars of pressure.

iii) Measuring optical properties

Opacity of the laminates is measured by evaluating the contrast ratio for each of the papers to be tested between the area on the kraft substrate and the area on the white substrate, using the "opacity" function of the Datacolor Elrepho 2000 spectrophotometer.

EXAMPLE 1

Preparation of a compound of mixed mineral conglomerates according to the invention in aqueous suspension form

RL62 is used in aqueous suspension form, titrating 40 g/l.

Mineral conglomerates are generated by heterocoagulation of the TiO₂ particles with silica aggregates.

The heterocoagulation process consists of adding silica slurry at a regulated pH in the bottom of an agitated tank containing the TiO₂ suspension. The pH of the heterocoagulation can be between 4.5 and 6.5, but it is preferable to

work at a pH = 5.5. The pH is regulated by simultaneously adding an HCl solution to the slurry. This operation takes place at ambient temperature. The final suspension contains 10% silica by mass compared to the content of TiO_2 pigment, and the overall dry extract ($\text{TiO}_2 + \text{SiO}_2$) is approximately 11%.

After 15 minutes of contact at a regulated pH of 5.5, the suspension, still under agitation, is brought to a temperature between 60°C and boiling for 1 to 3 hrs, then cooled to room temperature.

All samples prepared according to this protocol were tested by preparing test sheets (round sheets). For all tests, the volume of the "fiber + charge + PAE" mixture removed in the mixing tank was adjusted so as to obtain sheets with the same gram substance: 80 g/m².

- One section of the test sheet is calcined to determine the amount of oxide present in the dry sheet ($\text{SiO}_2 + \text{TiO}_2$). Knowing the amount of silica added in relation to TiO_2 , the % of TiO_2 present in the dry sheet is then calculated. The protocol for forming the test sheet and the principle for calculating the amount of TiO_2 are detailed in the previous section, "Materials and Methods".

By quantifying the TiO_2 and SiO_2 with X-ray fluorescence on the sheets obtained, it was verified that there was no preferred retention of one or the other kinds of minerals. The $\text{SiO}_2/\text{TiO}_2$ ratio was maintained throughout the entire sheet formation process.

- The other section of the test sheet is impregnated with resin and pressed in order to obtain a laminated paper for which opacity and whiteness are then measured. Protocols for impregnation and measuring opacity are also described above.

Some samples were also tested in the test sheet retention test to evaluate the congregates' resistance to shearing. This test consists of submitting the "fiber + charge + PAE" mixture to rapid agitation and shearing for a certain amount of time immediately before forming the test sheet.

The contribution of each of the two phenomena (retention and spacing effect) to the total increase in opacity measured for each of the tests is detailed in Tables 1 and 2.

Table 2 (following) also shows the results obtained with a control compound 1 (T1). It was prepared by simply mixing silica and TiO_2 .

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TABLE 1

Trial		Opacity					Ash Amount (% TiO ₂)	
No.	SiO ₂	Curing	Measures	Δ_{opa}	Δ_{ref}	Δ_{spac}	Measures	Δ_{ash}
1	0%	None	91.1	Ref.	Ref.	Ref.	35.6	Ref.
2	1%	3 hrs at boiling	92.0	+0.9	+0.6	+0.3	37.8	+2.2
3	5%	3 hrs at boiling	92.9	+1.8	+1.1	+0.7	39.9	+4.3
4	10%	3 hrs at boiling	92.8	+1.7	+1.0	+0.7	39.5	+3.9
5	10%	1 hr at boiling	93	+2.0	+1.1	+0.9	39.7	+4.1

TABLE 2

Trial No.	SiO ₂	Curing	Opacity (%)	Ash Amount (%)	Resin uptake (%)
6	0%	None	90.5	36.5	106
7	10%	1 hr at boiling	91.8	41.5	105
T1	10%	Simple mixture	89.5	39.5	130

Δ_{ash} = increase in amount of ash resulting from the best retention of TiO_2 during sheet formation.

Δ_{opa} = $\Delta_{ret} + \Delta_{spac}$ = increase in total opacity

Δ_{ret} = $\Delta_{ash} \times \text{slope}$ = increase in opacity resulting from the increase in amount of TiO_2 retained in the sheet (better retention).

Δ_{spac} = $\Delta_{opa} - \Delta_{ret}$ = increase in opacity resulting from the better dispersion of the TiO_2 retained in the sheet due to the spacing effect of the silica aggregates.

Results of tests 1 through 5 clearly show that the use of mixed mineral conglomerates makes it possible to not only improve retention at first pass (higher amount of ash), but also makes it possible to improve the opacity of the TiO_2 retained since in every case, the increase in opacity (Δ_{opa}) is greater than the increase in opacity normally expected with an increase in the quantity of ash (Δ_{ret}).

In contrast, a comparison of the results from control test 1 (T1) to those of tests 6 and 7 clearly reveals that a simple mixture, i.e., with no particular attention to the level of pH and curing conditions, does not result in any improvement in opacity.

The significant increase in the resin uptake is indicative of a porous and non-homogeneous structure.

As for the influence of the amount of silica, note that tests carried out with 5 and 10% silica were clearly more productive than the test conducted with 1% silica.

Consequently, the above results show that in comparison to a conventional formula (TiO_2 without silica), the use of a mixed mineral containing 5 and 10% silica should make it possible to increase opacity from 0.6 to 0.9 points with an equivalent rate of ash. This increase corresponds to the opacity rating measured for the highest performing test.

With these compounds according to the invention, it is also conceivable to use less TiO_2 while at the same time keeping the same opacity level as a conventional silica-free formula since the mixed minerals improve the amount of ash and opacity rate. The potential gain in TiO_2 can be estimated by evaluating the increase in the amount of ash corresponding to an increase in opacity equal to the opacity output. This value reported in the amount of ash in the silica-free tests

corresponds to the percentage of TiO_2 that can be saved while remaining at the same level of opacity as the control test. Under these conditions, using a mixed mineral containing 10% silica should allow a savings of at least 7 to 10% TiO_2 and still retain the same level of opacity as a conventional silicone-free formula.

EXAMPLE 2

Using the "test sheet retention" test, the product's retention capability obtained according to the invention was compared with that of "conventional" titanium oxides.

Product A:	produced according to the invention, $\text{SiO}_2 = 10\%$
Product B:	produced according to the invention, $\text{SiO}_2 = 15\%$
Product C:	TiO_2 , Rhoditan RO18
Product D:	TiO_2 , Rhoditan RL62

Results of the "test sheet retention" test are given in Table 3.

At a PAE rate of 0.8%, a standard rate in this application, products according to the invention result in retention rates that are superior to that of RL62 and equivalent to that of RL18. This is due to their anionic property as well as to the particular structure contributed by the synthesis process that is the object of the invention.

At a PAE of 0%, the self-retaining character of the product becomes evident. While more anionic than the RL18, the products according to the invention present a much more pronounced autoretention character. This is obvious proof of a particular geometric structure formed of loose congregates that are not very dense and in that case demonstrates that retention is far from being solely the result of electrostatic interactions between the fibers (naturally ionic) and the charges.

TABLE 3

Ref. Product	Amount of PAE (% dry/fibers)				
	0	0.2	0.4	0.8	1.2
	Rate of Retention (%)				
A	38	64	74	72	73
B	24	46	55	69	73
C	2.5 [sic]	36	44	79	74
D	49	57	47	40	42

EXAMPLE 3**Determining the Influence of the curing phase**

a) Effects in terms of retention:

Resistance to shearing of certain mineral conglomerate compounds identified in Example 1 was tested using the "retention sheet test".

Figure 3 shows the change in charge retention for different compounds as a function of agitation speed imposed on the "cellulose/PAE/charge" mixture prior to the formation of the fiber mat.

It is obvious that mixed mineral conglomerate retention decreases as agitation speed increases. It nonetheless remains clearly higher than that obtained with the silica-free charge. We can thus conclude that the mixed mineral conglomerates are sufficiently resistant to shearing to preserve good retention at first pass.

Results obtained also demonstrate that:

- reduction in curing time from 3 hrs to 1 hr has little influence on the resistance of the conglomerates.
- the system containing 10% silica provides better retention than the system containing 5% silica, irrespective of agitation speed. This result confirms that it is preferable to use 10% silica.

b) Effects in terms of opacity

It has been proven, in fact, that it is not possible to obtain a sheet of paper of good quality with an RL62 SiO₂ mixture with 10% SiO₂ that has not undergone the curing step.

As soon cellulose and PAE are added in the mixing tank, agglomeration and "balling" are encountered.

The curing step is thus a step essential to the formation of effective mixed mineral conglomerates.

EXAMPLE 4

Effect of mixed mineral conglomerates according to the invention on the whitening of laminated sheets of paper

The whiteness of laminated sheets (measured on the white background area) was measured for each trial. Results are summarized in Table 4, following.

Whiteness measurements were performed according to the CIE l* a* b* scale using a Datacolor Elrepho 2000® spectrophotometer.

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TABLE 4

Trials			Whitening			
No.	SiO ₂	Curing	L*	ΔL^*	b*	Δb^*
1	0%	None	93.8	Ref.	5.0	Ref.
2	1%	3 hrs at boiling	93.9	+0.1	4.7	-0.3
3	5%	3 hrs at boiling	94.0	+0.2	4.5	-0.5
4	10%	3 hrs at boiling	94.3	+0.5	4.4	-0.6
5	10%	1 hrs at boiling	94.1	+0.3	4.4	-0.6

It can be observed in general that the use of compounds in accordance with the invention improves the whiteness of the laminated sheet, even more so as the amount of silica increases. With 5 and 10% silica, a gain of approximately 0.2 points in L^* is measured and a decrease in b^* of from 0.4 to 0.6 points. This decrease in b^* gives a pronounced blue undertone to the laminated sheet which reinforces the impression of whiteness.

In addition to improving the retention and opacity rate from the TiO_2 retained, they also result in an improvement in the whiteness of the laminated sheet.

EXAMPLE 5

Preparation of a mixed mineral conglomerate compound in powder form

In this example, heterocoagulation is realized according to the procedure described in Example 1. After the curing step (1 hr at $90^\circ C$), the product is dried in a thin layer (15 hrs in drier at $150^\circ C$). The product obtained is divided into two parts. One is used as is, while the other is ground with air blasts (micronization).

Both of these products undergo an opacity test. They are used on cellulose fibers after placement in a slurry at 40% dry extract. They are then compared with a control product: Rhoditan RL62 titanium oxide placed into slurry at 40%. The formula used in this example is:

Cellulose fiber: 100 parts (15 g)

Opacifying pigment: 100 parts (15 g)

PAE resin: 0.8% dry/fibers

For the control product, 15 g of RL62 TiO_2 was introduced. For products in accordance with the invention, 15 g of the $TiO_2 + SiO_2$ combination was introduced.

The rest of the operating method is the same as that described in the "Opacity Rate" test.

Results are given in Table 5.

These results clearly demonstrate that a product made according to the invention subjected to a single drying (Test 2) is not superior to a standard product (Trial 1). On the other hand, after a micronization step (Test 3), all the potential for

improvement in opacity for this same product is brought out. In fact, it results in a sheet of paper which, after lamination, delivers opacity that is 2.4 points greater than that of the laminated paper developed from the reference product Rhoditan RL62, and with a completely comparable amount of TiO_2 in the sheet.

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TABLE 5

Trial No.	SiO ₂	Curing	Drying in Drier	Micronization	Opacity (%)	Amount of Ash (%)	Amount of TiO ₂ (%)
1	0%	-	-	-	89.1	38.2	38.2
2	10%	1 hr at 90°C	15 hr at 150°C	no	89.3	41.6	37.8
3	10%	1 hr at 90°C	15 hr at 150°C	yes	91.5	41.6	37.8

CLAIMS

1. Process for the preparation of a TiO_2 -based compound for use as an opacifier, including steps according to which:

- an aqueous dispersion of at least one inorganic spacer is mixed into an aqueous dispersion of TiO_2 , with the mixture of the two dispersions performed under agitation and at a pH between the respective isoelectric points of the TiO_2 and the spacer and selected such that the TiO_2 and the spacer have opposite and sufficiently different surface charges to result, under the effect of electrostatic forces, in their arrangement into mixed mineral congregates in which the TiO_2 particles are globally spaced away from each other by the particles and/or aggregates of the spacer;

- as necessary, the pH is adjusted to the value established in Step 1;

with said process characterized in that it also includes the steps according to which:

- the resultant aqueous dispersion of mixed mineral congregates is cured at a temperature sufficient to reinforce the solidity of the bonds established between the TiO_2 particles and the particles and/or aggregates of the spacer;

- the compound is recovered in the form of an aqueous dispersion of mixed mineral congregates, and

- the compound can possibly be formulated in dry form.

2. Process according to claim 1, characterized in that the titanium dioxide used is a rutile TiO_2 .

3. Process according to claim 1 or 2, characterized in that the titanium dioxide used is a rutile TiO_2 of pigmentary size.

4. Process according to claim 1, 2, or 3, characterized in that the TiO_2 is coated with a mineral surface treatment.

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5. Process according to claim 4, characterized in that the surface treatment contains at least one compound selected from among alumina, silica, zirconia, phosphate, cerium oxide, zinc oxide, titanium oxide, and mixtures thereof.

6. Process according to one of claims 1 through 5, characterized in that the aqueous dispersion of TiO_2 contains approximately 5 to 80 wt-% of TiO_2 .

7. Process according to claim 6, characterized in that the aqueous dispersion of TiO_2 contains approximately 5 to 40 wt-% of TiO_2 .

8. Process according to one of claims 1 through 7, characterized in that the inorganic spacer is selected from among silicon, titanium, zirconium, zinc, magnesium, aluminum, yttrium, antimony, cerium, and tin oxides; barium and calcium sulfates; zinc sulfide; zinc, calcium, magnesium, lead, and mixed metal carbonates; aluminum, calcium, magnesium, zinc, cerium, and mixed metal phosphates; magnesium, calcium, aluminum, and mixed metal titanates; magnesium and calcium fluorides; zinc, zirconium, calcium, barium, magnesium, mixed alkaline-earth, and silicated mineral silicates; alkaline and alkaline-earth aluminosilicates; calcium, zinc, magnesium, aluminum, and mixed metal oxalates; zinc, calcium, magnesium, and alkaline-earth aluminates; aluminum hydroxide, and mixtures thereof.

9. Process according to one of claims 1 through 8, characterized in that the inorganic spacer is selected from among silicon, zirconium, aluminum, antimony, cerium, and tin oxides, and mixtures thereof.

10. Process according to one of claims 1 through 9, characterized in that the inorganic spacer is used at a rate of approximately 1 to 40 wt-% in relation to the weight of the TiO_2 .

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11. Process according to one of claims 1 through 10, characterized in that the inorganic spacer is used at a rate of approximately 5 to 15 wt-% in relation to the weight of the TiO_2 .

12. Process according to one of claims 1 through 11, characterized in that the TiO_2 is a cationic pigmentary rutile TiO_2 .

13. Process according to claim 12, characterized in that the inorganic spacer is a silica, an alumina, a silicoaluminate, or a mixture thereof.

14. Process according to one of claims 1 through 13, characterized in that the inorganic spacer is a silica and that the TiO_2 is a cationic pigmentary rutile TiO_2 .

15. Process according to claim 14, characterized in that the silica has a specific surface of between approximately 20 and 300 m^2/g .

16. Process according to claim 14 or 15, characterized in that the silica occurs in the form of aggregates of a size between approximately 0.5 and 10 μm .

17. Process according to one of claims 14 through 16, characterized in that the silica is generated *in-situ* through the acidification of a solution of silicates.

18. Process according to claim 17, characterized in that the pH is adjusted after *in-situ* precipitation of the silica to a value favorable to the manifestation of electrostatic forces between the TiO_2 and the silica thus generated.

19. Process according to one of claims 14 through 17, characterized in that the two aqueous dispersions are brought together at a pH on the order of 5.5.

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20. Process according to one of claims 14 through 19, characterized in that the silica is used at a rate of approximately 5 to 15 wt-% in relation to the TiO_2 weight.

21. Process according to one of claims 14 through 20, characterized in that the curing step is performed at a temperature between 60°C and 100°C for at least 30 minutes.

22. Process according to one of claims 1 through 21, characterized in that the mixed mineral congregates obtained from the first or second step undergo mineral surface treatment.

23. Process according to claim 22, characterized in that the mineral surface treatment represents approximately 16 wt-% or less in relation to the total weight of the mixed mineral congregates treated.

24. TiO_2 -based compound obtainable by means of the process defined according to one of claims 1 through 23.

25. TiO_2 - and SiO_2 -based compound, characterized in that the TiO_2 and SiO_2 particles are arranged therein in the form of mixed mineral congregates with a TiO_2 and SiO_2 base in which the TiO_2 particles are globally spaced away from each other by aggregates of said silica.

26. Compound according to claim 25, characterized in that the silica occurs at a rate of approximately 5 to 15 wt-% in relation to the TiO_2 .

27. Compound according to claim 25 or 26, characterized in that the TiO_2 is a cationic pigmentary rutile TiO_2 .

28. Compound according to one of claims 25 through 27, characterized in that the silica has a specific surface of between approximately 20 and $300 \text{ m}^2/\text{g}$ and/or occurs in

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the form of aggregates of a size between approximately 0.5 and 10 μm .

29. Compound according to one of claims 25 through 28, characterized in that the TiO_2 - and SiO_2 -based mixed mineral conglomerates are coated with a mineral surface treatment.

30. Compound according to claim 29, characterized in that this mineral surface treatment represents approximately 16 wt-% or less in relation to the total weight of the mixed mineral conglomerates.

31. Use of a compound obtained according to one of claims 1 through 23 or a compound defined according to one of claims 24 through 30 as an opacifier.

32. Use according to claim 31 in the paper, plastics, and paint industries.

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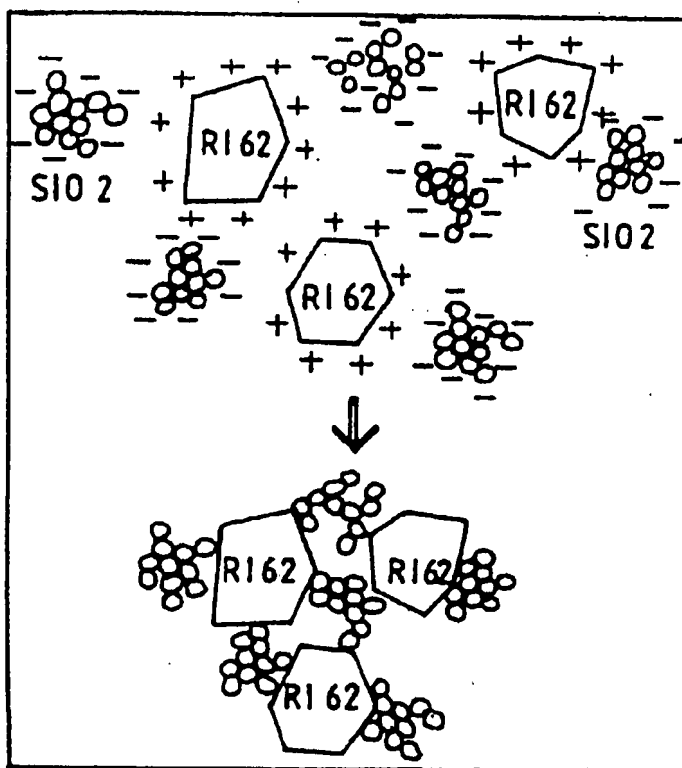


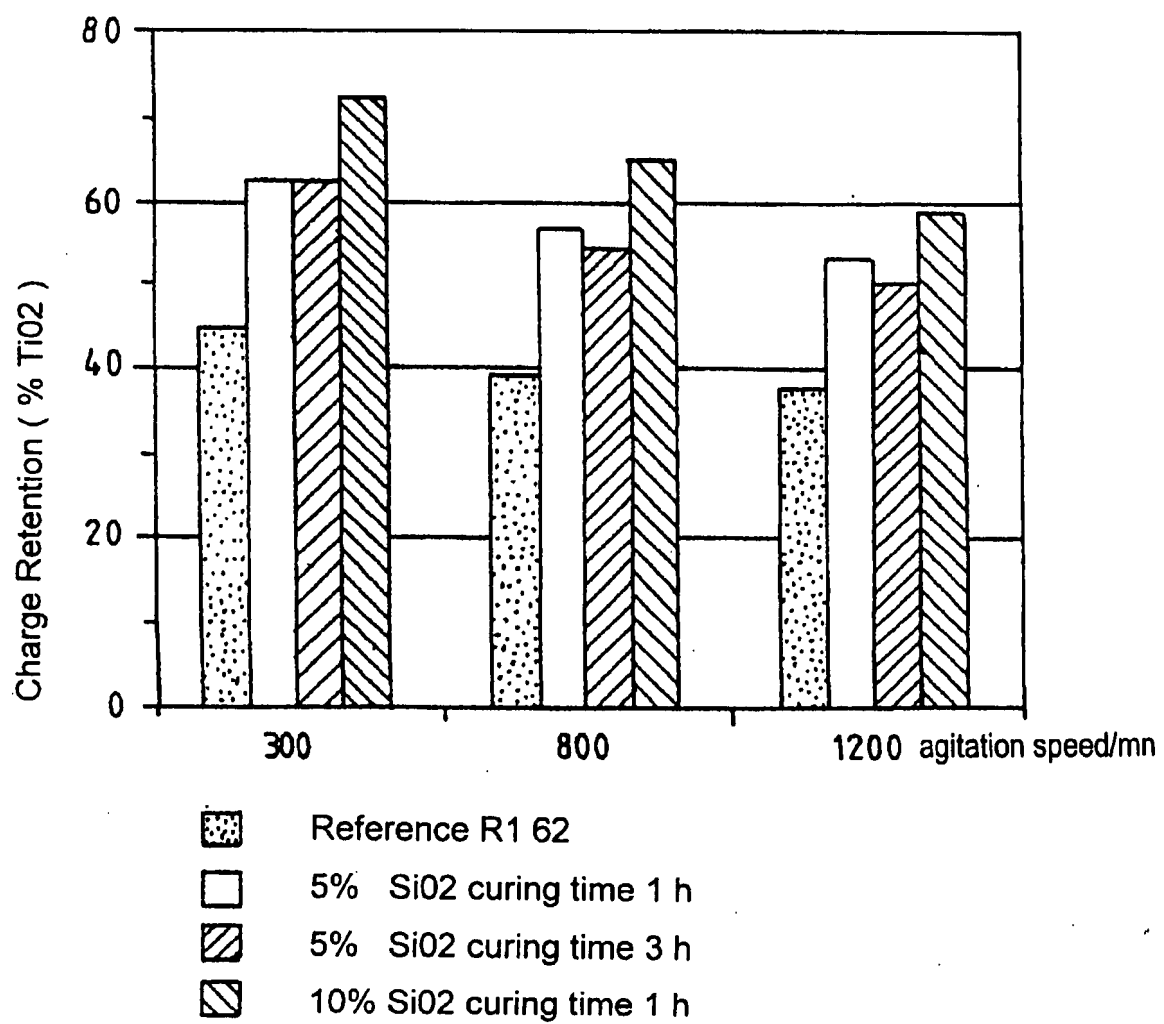
FIG.1

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FIG. 2

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FIG. 3